Simultaneous separation of common mono- and divalent cations on an acid-treated silica gel column by ion chromatography with indirect photometric detection and tyramine–oxalic acid, containing 18-crown-6 as eluent

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Abstract

The application of unmodified silica gel (Super Micro Bead Silica Gel B-5, SMBSG B-5) as cation-exchange stationary phase in ion chromatography with indirect photometric detection for common mono- and divalent cations (Li^+, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) was carried out using 0.75 mM tyramine [4-(2-aminoethyl)phenol]–0.25 mM oxalic acid at pH 5.0 as the eluent. Although complete group separation between these mono- and divalent cations was achieved on the SMBSG B-5 column (150×4.6 mm I.D.) in 12 min, peak shapes of NH_4^+ and K^+ were strongly tailed. Hence, the application of SMBSG B-5 silica gel treated with conc. hydrochloric acid at reflux-temperature for 12 h for the simultaneous separation of these cations was carried out. Although the retention volumes of these cations decreased on the acid-treated SMBSG B-5 silica gel column, the peak shapes of NH_4^+ and K^+ were quite improved. Excellent simultaneous separation and highly sensitive detection at 275 nm [detection limits (signal-to-noise ratio of 3 and injection volume of 20 μl), 0.34 μM for Li^+, 0.47 μM for Na^+, 0.39 μM for NH_4^+, 0.59 μM for K^+, 0.24 μM for Mg^{2+} and 0.28 μM for Ca^{2+}] were achieved in 15 min on the acid-treated SMBSG B-5 column using 0.5 mM tyramine–0.2 mM oxalic acid–10 mM 18-crown-6 (1,4,7,10,13,15-hexaoxacyclooctadecane) at pH 5.5 as the eluent. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Mobile phase composition; Stationary phases, LC; Inorganic cations; Tyramine; Crown ethers

1. Introduction

Ion chromatography with indirect photometric detection (IC-IPD) offers a simple and convenient method for the determination of inorganic and organic anions and cations [1]. In IC-IPD, analyte ion is detected indirectly, based on the difference in molar extinction coefficient between eluent ion and analyte ion. Various inorganic and organic cations were evaluated as eluent ions in IC-IPD for cations. The copper(II) ion is widely employed as the eluent ion in IC-IPD for cations. This is because the simultaneous separation of common mono- and divalent cations (Li^+, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) can be achieved easily on both sulfonated styrene–divinylbenzene (PS–DVB) co-polymer resin and sulfonated silica columns [2]. However, due to the low UV absorbance, the detection sensitivities of

these cations are moderate. Furthermore, the determination of these cations is often affected by organic compounds co-existing in analytical samples, because of the detection wavelength at 220–240 nm.

Protonated aromatic monoamines (PAMAs) with high UV absorbance were also evaluated as the eluent ions in the IC-IPD for cations. Haddad and Foley have applied various PAMAs as the eluent ions in IC-IPD with lightly sulfonated PS–DVB resin column for the separation of various cations [3]. Although highly sensitive detection was achieved, the simultaneous separation of common mono- and divalent cations could not be achieved.

Since silanol group on the surface of silica gel acts as a weak acid at pK_a of ca. 7.1 [4], unmodified silica gel was evaluated as a cation-exchange stationary phase in IC with conductimetric detection (CD) for cations [5–9]. The greatest advantage of IC-CD is that the simultaneous separation of major mono- and divalent cations (Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) could be achieved using lithium ion (Li^+) as the eluent ion [8,9], because the affinity of these mono- and divalent cations to the dissociated silanol group as cation-exchanger is very similar. These results indicated that unmodified silica gel was one of the most suitable cation-exchange stationary phases in the IC-IPD using PAMAs as the eluent ions. However, the application has not been so popular. This might be because commercially available silica gels, except for pure silica gel synthesized by the hydrolysis of pure tetraethoxysilane [$Si(OCH_2CH_3)_4$], contain various polyvalent metals as impurities and, consequently, undesirably strong interaction occurs between PAMAs and polyvalent metals on the surface of silica gel [10–13].

The aim of this study was to extend the utility of silica gel as the cation-exchange stationary phase in IC for cations. Then, the application of silica gel (Super Micro Bead Silica Gel B-5, SMBSG B-5) treated with conc. hydrochloric acid at reflex temperature for 12 h in IC-IPD for the simultaneous separation of common mono- and divalent cations (Li^+, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) was carried out using protonated tyramine [4-(2-aminoethyl)phenol] as eluent ion. Peak shapes of NH_4^+ and K^+ were strongly tailed on the SMBSG B-5 silica gel column, whereas symmetrical peaks of these cations were obtained on the acid-treated SMBSG

B-5 silica gel column. Excellent simultaneous separation and highly sensitive detection at 275 nm were achieved in 15 min on the acid-treated SMBSG B-5 silica gel column (150×4.6 mm I.D.) using 0.5 mM tyramine–0.2 mM oxalic acid–10 mM 18-crown-6 (1,4,7,10,13,15-hexaoxacyclooctadecane) at pH 5.5 as the eluent.

2. Experimental

2.1. Instruments

The ion chromatograph consisted of a Tosoh (Tokyo, Japan) LC-8020 chromatographic data processor, a Tosoh CCPM-II-R solvent delivery pump operating at a flow-rate of 1 ml min^{-1}, a Tosoh UV-8020 UV–Vis spectrophotometric detector operating at 275 nm, a Tosoh CO-8020 column oven operating at 35 °C, a Tosoh DS-8023 on-line degasser and a Reodyne (Cotati, CA, USA) Model 9125 injector equipped with 20 or 50 μl of sample loops.

A Toa Denpa (Tokyo, Japan) IM-40S ion meter with a glass electrode was used for the measurements of the pH of eluents and natural water samples.

2.2. Silica gels columns

A Fuji-Silysia Chemical (Kasugai, Japan) Super Micro Bead Silica Gel B-5 (SMBSG B-5, lot. No. 902530) porous spherical silica gel for HPLC was used in this work. A 10 g amount of the SMBSG B-5 silica gel was treated with 100 ml of conc. hydrochloric acid at reflux temperature for 12 h.

Table 1 shows the analytical results of polyvalent metals in these silica gels. The determination of these metals was carried out using a Nippon Jarrel-

Table 1
Analytical results of metals in Super Micro Bead Silica Gel B-5 silica gels by IEP-AES

Treatment	$\mu g\ g^{-1}$ Silica gel					
	Al	Ca	Fe	Mg	Ti	Zr
No treatment	30	8.9	7.1	1.5	93	13
Acid treatment	13	2.4	4.4	0.5	32	4.5

Table 2
Physical properties of Super Micro Bead Silica Gel B-5 silica gels

Treatment	Dry temperature (°C)	Particle size (μm)	Surface area ($m^2 g^{-1}$)	Pore size (Å)	Pore volume ($ml g^{-1}$)	Packing density ($g ml^{-1}$)	Surface area per column[a] ($m^2 column^{-1}$)
No treatment	200	5.9	417	60	1.04	0.45	5.1×10^2
Acid treatment	200	5.8	316	86	0.89	0.43	3.4×10^2

[a] Column size: 150×4.6 mm I.D.

Ash ICAP-1000 inductively coupled plasma atomic emission spectrometry (ICP-AES) system [14].

Table 2 shows the physical properties of the SMBSG B-5 and acid-treated SMBSG B-5 silica gels. The determination of the surface area and pore volume of these silica gels by using nitrogen adsorption isotherms on the gels at 77 K was carried out using a Beckman-Coulter (Fullerton, CA, USA) Omunisorp 360 gas sorption analyzer. The surface area was calculated from the BET equation. The determination of the particle size of these silica gels was carried out using a Horiba (Kyoto, Japan) LA-920 laser scattering particle size distribution analyzer.

The separation columns (150×4.6 mm I.D., stainless steel) were packed with these silica gels using the slurry packing method.

2.3. Chemicals

All chemicals were of analytical reagent grade. Tyramine [4-(2-aminoethyl)phenol], benzylamine, phenylethylamine and 18-crown-6 (1,4,7,10,13,15-hexaoxacyclooctadecane) were purchased from Aldrich (Milwaukee, WI, USA) and other chemicals were purchased from Wako (Osaka, Japan).

3. Results and discussion

3.1. Chromatographic behavior of mono- and divalent cations on SMBSG B-5 silica gel column using tyramine as eluent

Fig. 1 shows a chromatogram of common mono- and divalent cations (Li^+, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) on an unmodified silica gel (Super Micro Bead Silica Gel B-5, SMBSG B-5) column (150× 4.6 mm I.D.) obtained using 0.75 mM tyramine

[4-(2-aminoethyl)phenol]–0.25 mM oxalic acid at pH 5.0 as an eluent. The pH of eluent was adjusted using 0.1 M HNO_3.

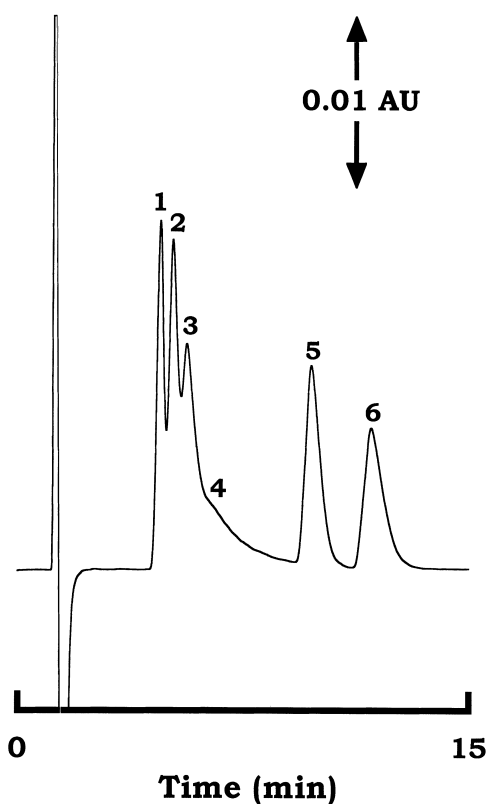As shown in Fig. 1, it was very easy to elute these

Fig. 1. Chromatogram of mono- and divalent cations on Super Micro Bead Silica Gel B-5 silica gel column obtained using protonated tyramine as eluent ion. Conditions: eluent: 0.75 mM tyramine–0.25 mM oxalic acid at pH 5.0, the pH of eluent was adjusted using 0.1 M HNO_3; flow-rate: 1 ml min^{-1}; column: Super Micro Bead Silica Gel B-5 (SMBSG B-5); column size: 150×4.6 mm I.D.; column temperature: 35 °C; detection: indirect UV at 275 nm; injection volume: 20 μl; sample concentration: 0.2 mM for monovalent cations and 0.1 mM for divalent cations. Peaks: 1=Li^+, 2=Na^+, 3=NH_4^+, 4=K^+, 5=Mg^{2+} and 6=Ca^{2+}.

mono- and divalent cations in a reasonable period of time (≤ 15 min). Unfortunately, peak shapes of NH_4^+ and K^+ were strongly tailed. The degree of peak destruction was $Li^+ < Na^+ < NH_4^+ < K^+$ and was in agreement with the elution order. In order to clarify the main cause of the peak destruction, IC behavior of these mono- and divalent cations on the SMBSG B-5 silica gel column was investigated using various protonated aromatic monoamines (tyramine, benzylamine, phenylethylamine, 2-methylpyridine and 2,6-dimethylpyridine) as the eluent ions. Chromatograms of these mono- and divalent cations obtained using these protonated aromatic monoamines as the eluent ions were almost no variation. As reported previously [15], since the SMBSG B-5 silica gel was successfully applied as the cation-exchange stationary phase in IC with conductimetric detection for these mono- and divalent cations using hydronium ion (H^+) as the eluent ion, it was expected that the main cause of the peak destruction could be attributed to strongly undesirable interaction between protonated aromatic monoamines and polyvalent metals present as impurities in the SMBSG B-5 silica gel.

3.2. Chromatographic behavior of mono- and divalent cations on acid-treated SMBSG B-5 silica gel column using tyramine as eluent

In order to reduce the undesirable interaction, acid treatment of silica gel was carried out [12,13]. The SMBSG B-5 silica gel was treated with conc. hydrochloric acid at reflux-temperature for 12 h for the removal of metals from the SMBSG B-5 silica gel. Table 1 shows the analytical results of metals in the SMBSG B-5 and acid-treated SMBSG B-5 silica gels. Table 2 shows the physical properties of the SMBSG B-5 and acid-treated SMBSG B-5 silica gels.

As shown in Table 1, more than 60% of the amount of polyvalent metals, except for Fe, was removed from the SMBSG B-5 silica gel. It was evident that the acid-treatment was a very effective way for the removal of metals in silica matrix. Fig. 2A shows the chromatogram of these mono- and divalent cations on the acid-treated SMBSG B-5 silica gel column. Peak shapes of NH_4^+ and K^+ were drastically improved. This result strongly confirmed

that the main cause of the peak destruction was attributed to strong interaction between protonated aromatic monoamines and polyvalent metals in the SMBSG B-5 silica gel. In contrast, the retention volumes of these cations decreased. This is because the SMBSG B-5 silica gel itself was somewhat dissolved in conc. hydrochloric acid and then the surface area decreased, as shown in Table 2. Unfortunately, the decrease caused the inferiority of the peak resolution between these mono- and divalent cations. Then, reasonable eluent conditions were investigated. As shown in Fig. 2B, since both complete group separation of these mono- and divalent cations and complete separation of the divalent cations were achieved on the acid-treated SMBSG B-5 column in 15 min, reasonable eluent conditions were decided to be 0.5 mM tyramine–0.2 mM oxalic acid at pH 5.5.

3.3. Effect of 18-crown-6 in eluent on chromatographic behavior of mono- and divalent cations on acid-treated SMBSG B-5 column

The acid treatment was very effective for the improvement of peak shapes of the monovalent cations in the IC-IPD conditions, whereas peak resolution between the monovalent cations on the acid-treated SMBSG B-5 column remained unsatisfactory. Then, in order to separate these mono- and divalent cations completely on the acid-treated SMBSG B-5 silica gel column, 18-crown-6 (1,4,7,10,13,15-hexaoxacyclo octadecane) was added to the eluent (0.5 mM tyramine–0.2 mM oxalic acid at pH 5.5). Fig. 3 shows the relationship between the concentration of 18-crown-6 in the eluent and the retention volumes of these mono- and divalent cations.

As for the monovalent cations, with increasing the concentration of 18-crown-6 in the eluent, the retention volumes of Li^+ and Na^+ slightly decreased and the retention volume of NH_4^+ was almost no variation. In contrast, the retention volume of K^+ increased drastically at first and then slightly decreased. The degree of increase in the retention volumes was $Li^+ < Na^+ < NH_4^+ << K^+$. This order was in good agreement with that predicted from the stability constants of complexes formed between the monovalent cations and 18-crown-6 [16]. This result
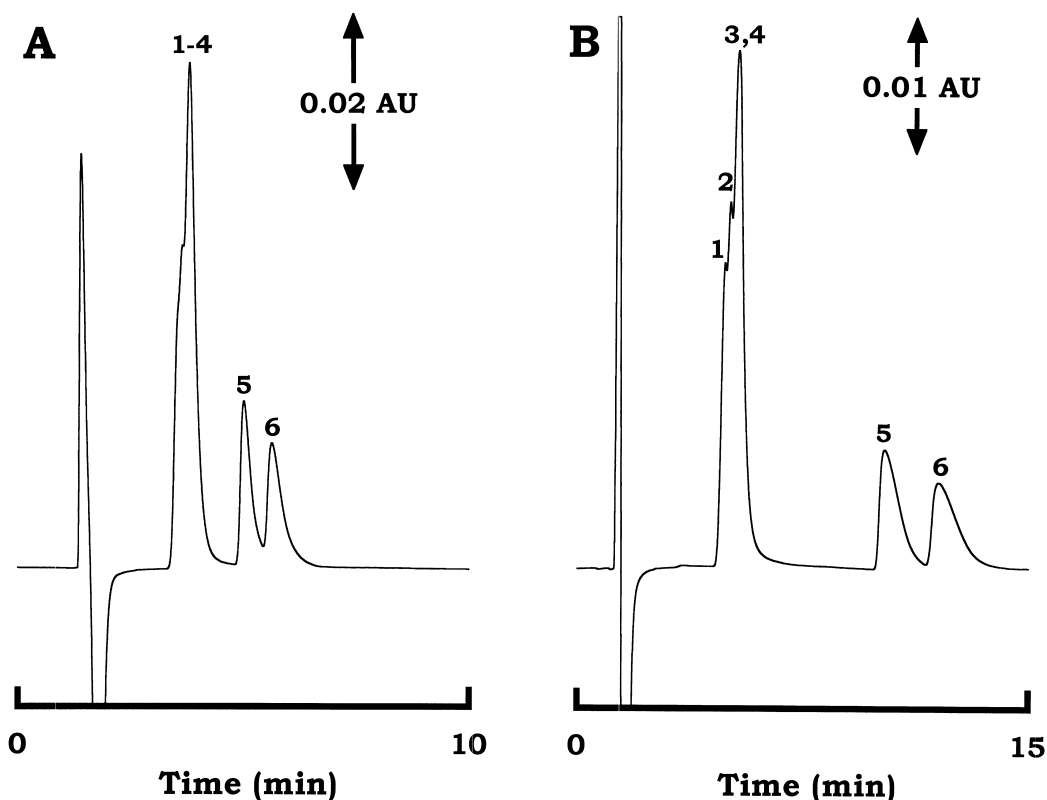
Fig. 2. Chromatograms of mono- and divalent cations on acid-treated SMBSG B-5 silica gel column obtained using protonated tyramine as eluent ion. Conditions: eluent: (A) 0.75 mM tyramine–0.25 mM oxalic acid at pH 5.0, (B) 0.5 mM tyramine–0.2 mM oxalic acid at pH 5.5, the pH of eluents was adjusted using 0.1 M HNO$_3$. Column: acid-treated SMBSG B-5. Other conditions as in Fig. 1.

indicated that18-crown-6 was adsorbed on the surface of the acid-treated SMBSG B-5 silica gel and acted as a selective cation-exchanger under the IC-IPD conditions. Complete separation of the monovalent cations was achieved at the concentration of 18-crown-6≥10 mM. As for divalent cations, the retention volumes decreased with increasing the concentration of 18-crown-6 in the eluent. This is due mainly to low stability of complexes formed between the divalent cations and 18-crown-6 [16] and perhaps due to a decrease in the cation-exchange capacity of the acid-treated SMBSG B-5 silica gel caused by increasing the amount of 18-crown-6 adsorbed on the silica gel. Complete group separation of these mono- and divalent cations was achieved at the concentration range of 18-crown-6 between 0 and 10 mM.

As shown in Fig. 4, excellent simultaneous sepa-

ration of these mono- and divalent cations on the acid-treated SMBSG B-5 silica gel column was achieved in 12 min by elution with 0.5 mM tyramine–0.2 mM oxalic acid–10 mM 18-crown-6 at pH 5.5.

3.4. Analytical performance parameters

Table 3 shows the detection limits (signal-to-noise ratio of 3) of these mono- and divalent cations. Highly sensitive detection was achieved in the IC-IPD. The detection limits were much lower than those obtained by IC with conductimetric detection using both unmodified silica gels as the cation-exchange stationary phases and lithium ion (Li$^+$) as the eluent ion [9].

Calibration graphs were obtained by plotting the chromatographic peak area against the concentration
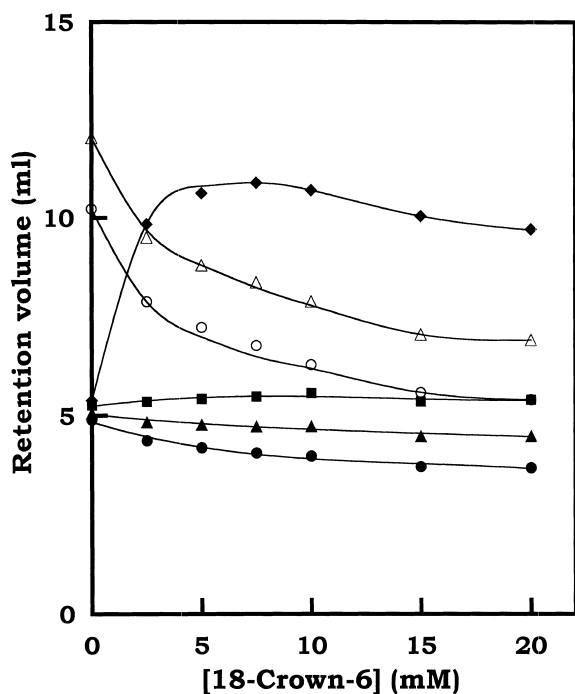
Fig. 3. Effect of concentration of 18-crown-6 in eluent on retention volumes of mono- and divalent cations on acid-treated SMBSG B-5 silica gel column. Conditions: eluent: 0.5 mM tyramine–0.2 mM oxalic acid at pH 5.0 containing 0–20 mM 18-crown-6. Symbols: ●=Li$^+$; ▲=Na$^+$; ■=NH$_4^+$; ♦=K$^+$; ○= Mg^{2+}; △=Ca^{2+}. Other conditions as in Fig. 2.

Fig. 4. Chromatogram of mono- and divalent cations on acid-treated SMBSG B-5 silica gel column obtained using 0.5 mM tyramine–0.2 mM oxalic acid–10 mM 18-crown-6 at pH 5.5 as eluent. Other conditions as in Fig. 3. Peaks: 1=Li$^+$, 2=Na$^+$, 3=NH$_4^+$, 4=K$^+$, 5=Mg^{2+} and 6=Ca^{2+}.

of these mono- and divalent cations. Linear calibration graphs ($r^2 \geq 0.99$) were obtained in the concentration range between 0.005 and 1.0 mM for these mono- and divalent cations.

The relative standard deviations of the chromatographic peak areas of these mono- and divalent cations, whose concentrations were 0.2 mM for the monovalent cations and 0.1 mM for the divalent cations, were less <0.8% (n=10). Reproducible chromatograms were obtained during repeated chromatographic runs.

3.5. Application to separation of major cations in natural water samples

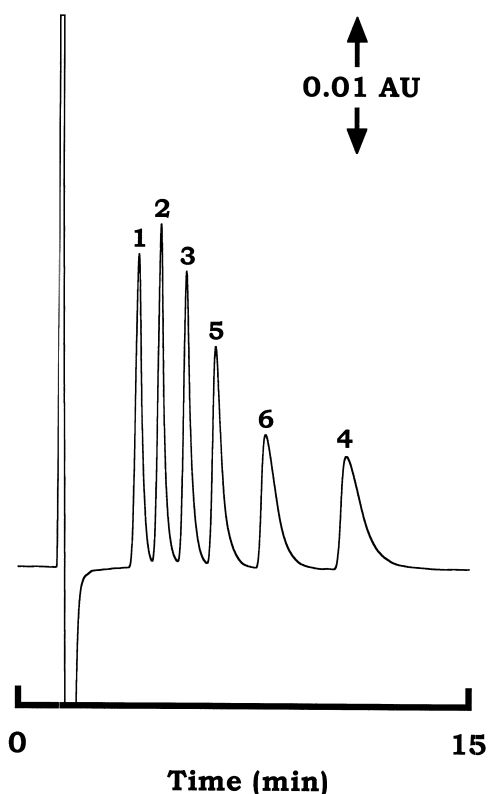The proposed IC-IPD method was applied to the determination of major mono- and divalent cations

(Na$^+$, NH$_4^+$, K$^+$, Mg^{2+} and Ca^{2+}) in river and rain water samples. Samples were analyzed after filtration through a 0.45 μm membrane filter. Fig. 5A and B

Table 3
Detection limits of common mono- and divalent cations

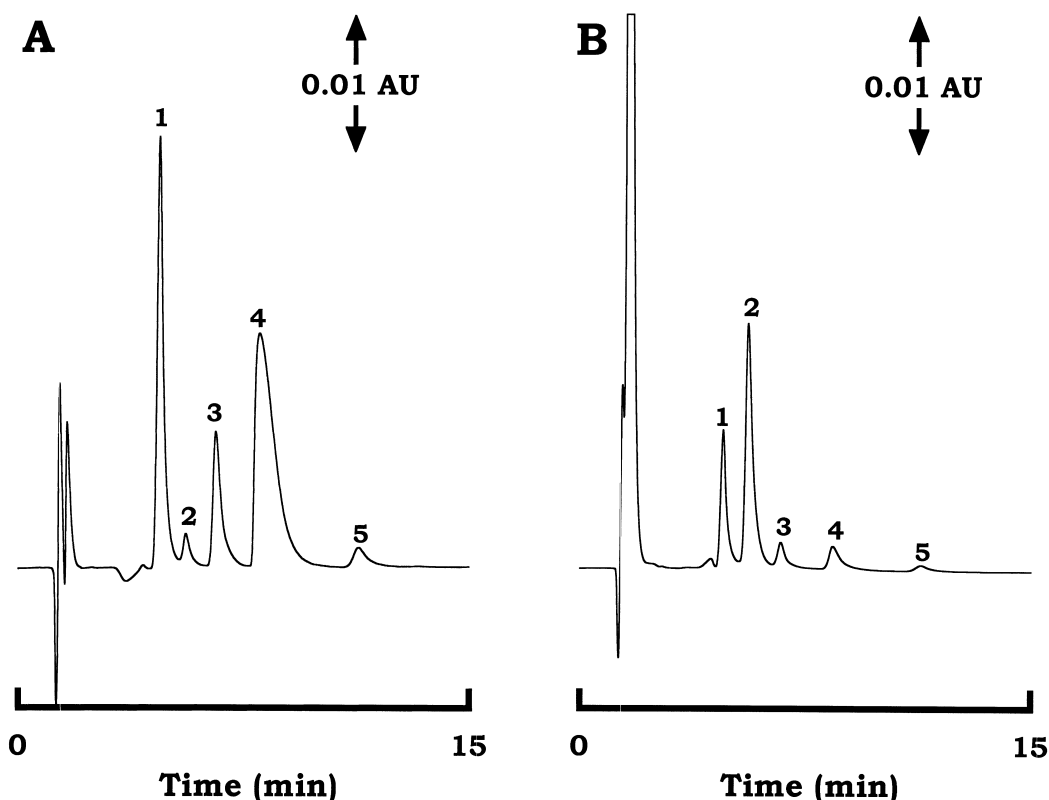| Cation	Detection limit	
	μM	ng ml^{-1}
Li$^+$	0.34	2.3
Na$^+$	0.47	11
NH$_4^+$	0.39	7.0
K$^+$	0.59	23
Mg^{2+}	0.24	6.0
Ca^{2+}	0.28	11

Signal-to-noise ratio of 3. Injection volume 20 μl.

Fig. 5. Chromatograms of river and rain water samples. (A) River water (injection volume of 20 μl); peaks (concentration, mM): 1=Na$^+$ (0.26), 2=NH$_4^+$ (0.02), 3=Mg^{2+} (0.06), 4=Ca^{2+} (0.21) and 5=K$^+$ (0.02). (B) Rain water (injection volume of 50 μl); peaks (concentration, mM): 1=Na$^+$ (0.025), 2=NH$_4^+$ (0.043), 3=Mg^{2+} (0.007), 4=Ca^{2+} (0.014) and 5=K$^+$ (0.003).

show chromatograms of river and acid rain water samples, respectively.

As shown in Fig. 5A, it was easy to successfully apply the IC-IPD for the determination of these mono- and divalent cations in the river water sample at injection volume of 20 μl. In contrast, the accurate determination of these cations, especially K$^+$, in the rain water sample was very difficult by the proposed IC-IPD at the injection volume at 20 μl, because the concentrations of these cations was considerably lower than those in the river water sample. However, as shown in Fig. 5B, the IC-IPD was successfully applied for the determination of these mono- and divalent cations in the rain water sample at the injection volume of 50 μl.

From these above results, it was proved that the proposed IC-IPD was a very useful method for the

determination of major cations in natural water samples.

4. Conclusion

In this work, the application of commercially available silica gel (Super Micro Beads Silica Gel B-5, SMBSG B-5) as a cation-exchange stationary phase in IC-IPD for common mono- and divalent cations (Li$^+$, Na$^+$, NH$_4^+$, K$^+$, Mg^{2+} and Ca^{2+}) was carried out using protonated tyramine [4-(2-amino-ethyl)phenol] as an eluent ion. Peak shapes of NH$_4^+$ and K$^+$ were strongly tailed on the SMBSG B-5 column under the IC-IPD conditions. The main cause of the peak destruction might be attributed to poly-valent metals present as impurities in the SMBSG

B-5 silica gel. Then, in order to remove polyvalent
metals, the SMBSG B-5 silica gel was treated with
conc. hydrochloric acid at reflux-temperature for 12
h. Excellent simultaneous separation and highly
sensitive detection at 275 nm for these mono- and
divalent cations were achieved in 12 min on the
acid-treated SMBSG B-5 silica gel column (150×4.6
mm I.D.) using 0.5 m*M* tyramine–0.2 m*M* oxalic
acid–10 m*M* 18-crown-6 (1,4,7,10,13,15-hexaox-
acyclooctadecane) at pH 5.5 as the eluent. The result
indicated that the acid-treatment was an easy and
effective way for the preparation of advanced cation-
exchange stationary phases for IC-IPD using proton-
ated aromatic monoamines as the eluent ions. These
results extend largely the utility of conventional
silica gel as the cation-exchange stationary phase in
IC for cations.

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